Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 934

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February 2002

Submitted to
TAPPI Journal

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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Abstract

Small clay particles can agglomerate with polyvinyl acetate (PVAc) to form neutral-buoyancy aggregates. When clay is added to water and centrifuged, a measurable population of total suspended particles (TSS) are obtained. No significant change in TSS occurs when PVAc is added to the mixture at 45°C prior to centrifugation. Both components are heavier than water at this temperature, and any aggregation does not significantly change the number of suspended particles. However, centrifuging the clay-PVAc mixture at 60°C increases TSS, because the PVAc floats at this temperature, and aggregation of the now lighter PVAc with the heavier PVAc increases the quantity of neutral-buoyancy particles. The formation of aggregates is confirmed by electron microscopy and by particle size measurements. These aggregates will be transparent to centricleaners. Furthermore, since stickies will be spread on the surface of the particle, its surface area will increase. Hence, clay will increase the effective concentration of the stickie and will also decrease cleaning efficiency.

The efficiency of centrifugal cleaners depends principally on the size and specific gravity of the particles to be removed (1). Cleaners are used extensively in paper recycling, and their performance is frequently less than optimal, suggesting that other factors might come into play. A wide variety of contaminants ranging from heavy particles such as ink and clay to lighter materials such as organic adhesives are encountered. Typically, the heavy contaminants are removed more successfully than are the adhesives. In a survey of stickies from various process streams at two newsprint mills we found that clay was frequently associated with stickies even after passage through both forward and reverse cleaners (2). This was curious since clay has a specific gravity of 1.8 g/cm^3, and should have been easily removed. In this paper we demonstrate that clay can associate with polyvinyl acetate (PVAc) to form neutral-buoyancy aggregates that would be transparent to centricleaners.

Experimental

Polyvinyl acetate (MW 500,000) was obtained from Polysciences Inc. Kaolin clay (DB KOTE 2 Spray Dried) was acquired from Dry Branch Kaolin Company. A relationship (equation 1) between total suspended solids (TSS) and turbidity was established by preparing several suspensions of clay in water and measuring both TSS and turbidity.

$$\text{TSS (g/L)} = 0.0002 \text{ turbidity (NTU)} - 0.0015 \quad (r^2 = 0.92, n=4) \qquad (1)$$

No measurable turbidity was recorded from suspensions of only PVAc in water. A series of experiments was run where mixtures of clay (0.1-0.4%) and PVAc (0.2%) were added to water at various temperatures with stirring. TSS measurements (expressed as a percentage of solids in water) were made in triplicate. An aliquot was centrifuged in an insulated vessel (to maintain temperature) at 400 g for 15 minutes, and the turbidity measured and converted to TSS through equation (1). The uncertainty in TSS was about 7%. The stirring period did not affect the results, indicating that steady-state conditions are reached rapidly. No change in TSS was observed when a 0.4% clay and 0.2% PVAc mixture in water was stirred at 60°C for 0.5 to 4 hours. Hence, a stirring period of 30 minutes was used throughout. All measurements were made in triplicate.

For the electron microscopy work, a 0.4% clay suspension in water was centrifuged as above and PVAc (0.2%) added to the centrifugate at 70°C with stirring. The suspension was then filtered through an YM1 membrane (Millipore Corp., Bedford, MA), and images were taken of the residue with an JSM-6400 instrument. For the particle size measurements, suspensions of clay in water (0.1-0.4%) were centrifuged. PVAc (0.2%) was added, the suspension heated to 70°C with strong stirring. Particle size measured with a Malvern Zetasizer.

Results and Discussion

The specific gravity of PVAc in water is temperature-dependent (3); the polymer used in this study floats at temperatures above 50°C and sinks at cooler temperatures. We reasoned that if PVAc and clay (which is heavier than water) were added to water, then at high temperatures we would have one floating and one sinking component, whereas at temperatures below 50°C, both components would sink. Hence, there is a potential for neutral-buoyancy clay/PVAc agglomerates to develop in the former situation, but not in the latter.

Figure 1 compares the TSS of clay alone to that of mixtures of clay and PVAc at 60°C. The TSS of the mixture is substantially higher than those of the individual components. Similar results were obtained at 70 and 80°C. Contrasting results were obtained at 45°C and are illustrated in Figure 2. Here, the presence of PVAc makes no significant difference to the TSS. Interpretation of these results is straightforward. At the higher temperature, the light PVAc partially agglomerates with the heavy clay to form a neutral-buoyancy mixture. Both components are heavy at the lower temperature, and agglomeration does not bring the clay into suspension.

Clay is much heavier than water, and the TSS of the suspension derived from clay alone must be due to particles that are too small to be centrifuged down (4). It is likely that the adhesive coats the clay particles and reduces their specific gravity at the higher temperature. This brings a subset of the population into the neutral-buoyancy region. Increasing the quantity of clay relative to that of PVAc increases the subset affected. The difference in TSS in Figure 2 increases almost linearly with clay content, which suggests at least a quasi-equilibrium situation. A value of 0.0016 $g^{-1}L$ was calculated for the ratio [TSS]/[clay][PVAc]. We believe that this value is a measure of the sub-population that is brought to neutral buoyancy.

Aggregate formation should increase particle size, and measurements were first made on the centrifugate from suspensions of 0.1-0.4% clay in water. The results, presented in Figure 3 demonstrate that the particle size stabilizes at 269-270 nm. The particles grow in the presence of PVAc at 70°C in keeping with the formation of aggregates. In contrast, the 30°C profile is similar to that of clay alone. The differences in particle size are barely outside experimental uncertainty, but they are consistent with the TSS results in Figures 1 and 2. The particle size increases by a maximum of only 3% in Figure 3, and the aggregate is still much heavier than water. We believe that the clay particle of a size range just large enough to be centrifuged down in the absence of PVAc are brought into suspension through agglomeration with the polymer.

Finally, SEM images provide direct evidence for the association of PVAc and clay. Images of aggregates are compared to those of clay alone in Figure 4, and a relatively uniform coating of polymer on clay is visible. Considered together, our results demonstrate that clay associates with PVAc (and probably other stickies) and that a fraction of the aggregate is of neutral buoyancy and is transparent to centricleaners. This explains why clay and stickies can be found together downstream of the cleaners. Since the stickie coats the clay particles, the clay increases the effective concentration of the stickie, and mills that process high-ash furnish may find stickies control to be especially challenging.

Acknowledgments

This study was funded by the Member Companies of the Institute of Paper Science and Technology.

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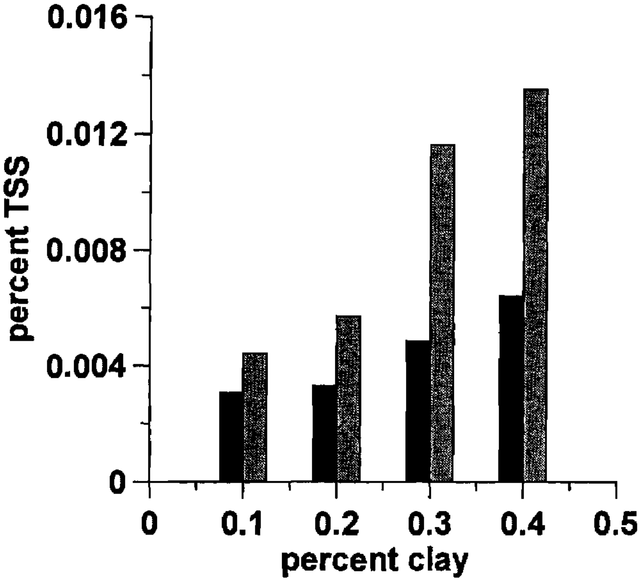

Figure 1: Effect of 0.2% PVAc on the TSS of clay in water at 60°C. The bold and hatched bars represents clay and the clay/PVAc mixture, respectively

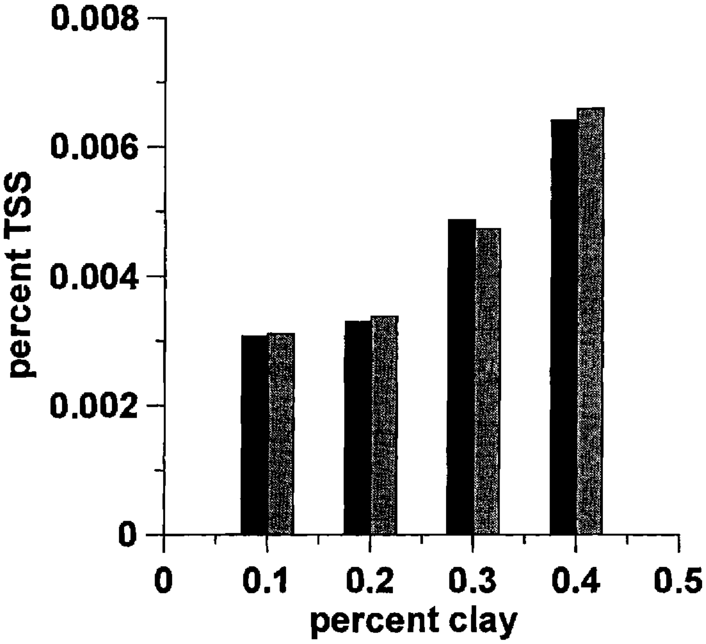

Figure 2: Effect of 0.2% PVAc on the TSS of clay in water at 45°C. The bold and hatched bars represents clay and the clay/PVAc mixture, respectively.

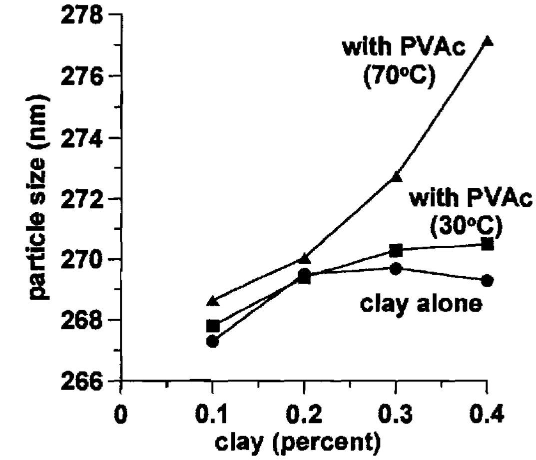

Figure 3: Particle size of solids in clay-PVAc centrifugate. The clay values reflect the quantities initially added.

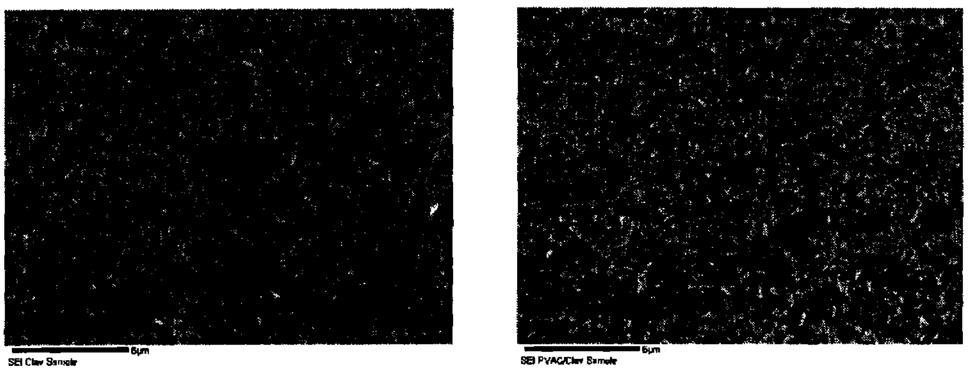

Figure 4. SEM images of clay (left) and clay-PVAc aggregates (right).